

Mineral Carbonation: A Viable Method for CO2 Sequestration

Program Plan and Approach

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Introduction

Today, world energy use is dominated by fossil fuels, which account for 80 - 85% of the total. The reasons for this include their abundant supply, high energy density, ease of use, ease of storage, existing infrastructure, acceptance by the public, and most importantly their low cost. The use of this important energy source is facing a challenge due to the vast amounts of CO₂ released into the atmosphere as a result of combustion. The level of CO₂ in the atmosphere has increased by roughly 30% since the

industrial revolution, with much of this rise being attributed to the increased use of fossil fuels such as coal, oil and natural gas (1,2). This change greatly exceeds natural fluctuations during the last few thousand years. Since 1800, the CO₂ content of the atmosphere has risen from a stable level of 280 ppm to above 365 ppm today. While the observation that the atmospheric CO₂ level has increased significantly is generally not at issue, the consequences arising from this increase are the subject of vigorous debate. Given that CO₂ is a greenhouse gas, such large and increasing atmospheric CO₂ levels will have climatic consequences, the exact extent of which is unknown. Unless action is taken, the emissions of CO₂ will continue to increase as the world economy grows, resulting in exponential growth of the level of atmospheric CO₂. Importantly, it would be very difficult and much more expensive to retract the dispersed CO₂ from the atmosphere at a later date when the consequences of increased levels are fully known. For these reasons, studies are actively pursuing solutions that can reduce atmospheric CO₂ emissions.

Improving the efficiency of energy production and energy utilization will certainly play a very important role in reducing CO₂ emissions. The DOE's Office of Fossil Energy is developing advanced power systems that promise efficiencies above 60%, almost a two-fold increase from today's averages. However, if global energy consumption increases by four-fold over the next century as some predict, with concomitant increases in carbon emissions, attainment of atmospheric CO₂ stabilization will require that sequestration technologies be employed on a large scale.

Historically, per capita energy consumption and wealth, as reflected by Gross Domestic Product (GDP), are nearly proportional. The U.S., followed closely by other highly industrialized nations, has a relatively high per capita energy consumption which is roughly equivalent to five times the global average. In considering this, it is important to note that it is the U.S.'s high per capita energy consumption that is directly responsible for its high standard of living. As the standard of living continues to rise globally and in developing countries in particular, it is not difficult to imagine that in the not too distant future the world will be using energy (and emitting CO₂) at many times today's rate. Over the 30-year period ending in 2020, projections made by the U.S. Energy Information Agency

indicate global increase in energy use will increase worldwide emissions of CO₂ to 38 10⁹ tons per year or an increase of 80% compared to 1990 levels (3).

The U.S. Department of Energy is also actively developing renewable energy sources that would not emit greenhouse gases. The use of renewable energy sources, however, remains very modest compared with total energy consumption because of various constraints. Given the public mandate to maintain economic growth, fossil fuels will remain a dominant energy source over the next century, as no alternative energy supply is poised to significantly replace fossil energy without causing other major problems. Therefore, developing effective CO₂ sequestration is one of the critical components in

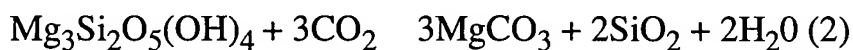
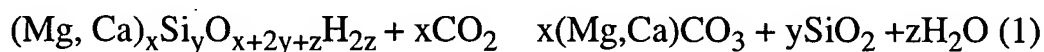
addressing global climate change. Even if renewable energy could reach 30% market penetration, fossil energy consumption would still need to grow.

The Department of Energy is conducting various CO₂ sequestration and recycling studies including underground storage (seabed- or land-based), ocean sequestration, biomass utilization, and using CO₂ as feed material to produce various environmentally benign products (4). Challenges to any solution include technical feasibility, economic viability, environmental soundness and long term sustainability. A balanced research portfolio exploring a number of both short and long term mitigation methods is therefore essential to ensure appropriate technology for individual circumstances. This paper focuses on the current status and future needs for research on one method of CO₂ sequestration: permanent CO₂ fixation as environmentally benign carbonate minerals. This effort is being conducted as part of Fossil Energy's Advanced Research and Technology Development efforts. The Mineral Sequestration Program is being managed by the Federal Energy Technology Center and is supported by the Coal Utilization Science (CUS), University Coal Research (UCR), and the Advanced Metallurgical Processes programs. The activities of the working group are being coordinated by the CUS program.

What is Mineral Sequestration

Mineral sequestration involves the reaction of CO₂ with minerals to form geologically stable carbonates, i.e. mineral carbonation. Since the resulting carbonates are thermodynamically stable solids, mineral sequestration is a process that can reduce CO₂ emissions to the atmosphere via permanent CO₂ disposal. For example, the reaction of CO₂ with common mineral silicates to form carbonates like magnesite or calcite is exothermic and thermodynamically favored under ambient conditions. The reaction is well known to geologists because it occurs spontaneously on geological time scales.

For illustrative purposes, general and specific global mineral carbonation reaction pathways are shown below. The family of reactions represented by Reaction 1 has the potential to convert naturally



occurring silicate minerals to geologically stable carbonate minerals and silica. This process emulates natural chemical transformations that occur spontaneously in nature (i.e., weathering of rocks to form carbonates over geologic time periods). Reaction 2 illustrates the transformation of the common silicate mineral serpentine, Mg₃Si₂O₅(OH)₄, and CO₂ into magnesite, MgCO₃, silica and water. Using this ideal case, one ton of serpentine can dispose of approximately one-half ton of CO₂.

Why Mineral Sequestration

The major benefits of CO₂ sequestration by mineral carbonation are:

Long Term Stability

Mineral carbonation is a natural process that is known to produce environmentally safe and stable material over geological time frames. The production of mineral carbonates insures a permanent fixation rather than temporary storage of the CO₂, thereby guaranteeing no legacy issues for future generations.

Vast Capacity

Raw materials for binding the CO₂ exist in vast quantities across the globe. Readily accessible deposits exist in quantities that far exceed even the most optimistic estimate of coal reserves (~10,000 10⁹ tons) (5).

Potential to be Economically Viable

The overall process is exothermic and, hence, has the potential to be economically viable. In addition, its potential to produce value-added by-products during the carbonation process, including energy, can further contribute to its cost effectiveness.

At a single site and scale that is consistent with current industrial practice, the process can easily handle the output of one to several large power plants. It is directly applicable to advanced power plants such as zero-emissions Vision 21 system configurations being developed by DOE's Fossil Energy Program or to existing power plants, thereby providing an additional degree of flexibility for future implementation(6).

Program Approach

Goals

The goal of the program is to develop a knowledge base for creating permanent and economical CO₂ mineral sequestration process(es). Program objectives include:

- i. identifying favored technical processes,
- ii. determining the economic feasibility of each sequestration process identified, and
- iii. determining the potential environmental impacts of each process.

Current State of Understanding

The use of Mg bearing silicates was first intensively investigated as a means to produce Mg metal during the first half of the 20th century (7-12). An aqueous process which utilized HCl digestion of minerals was found to be technically feasible and cost competitive for the time (10-11). Although the process was workable, specific problems identified were the loss of HCl, slow filtration rates (i.e., issues with separating the values from the gangue), issues related to the formation of gels, and the appropriate methods for the acid digestion which would be amenable to large scale processing (10). Despite these problems, pilot plant operations were conducted and successful (11). In 1990, ultramafic rocks (the generic name for Ca, Mg, Fe rich rocks; Amafic® meaning Mg, Fe, Ca-bearing rocks) were once again identified as a potential source for Mg and Ca (13). This time the suggestion was made to utilize these rocks as a means to sequester CO₂ rather than as a source of Mg metal. There have been several means suggested to achieve carbonation: an aqueous scheme by Kojima (14); an underground injection scheme by Gunter *et al.* (15,16); and most importantly, the processes suggested by Lackner *et al.* (17), which forms the basis for our program.

The research conducted at Los Alamos by Lackner *et al.* (18-26) (which includes the basic chemistry and availability of mineral deposits) during the past three years suggests the carbonation of magnesium and calcium silicates can viably adapt and use many of the processes described in the 40's.

Initial research focused entirely on the use of magnesium silicate ores in the magnesium hydroxide route to carbonation. The overall direct reaction is either the carbonation of forsterite,



or the carbonation of serpentine,



As can be seen from the equations, both reactions are exothermic; for comparison, the combustion of carbon yields 394 kJ/mole. Most importantly, both reactions are thermodynamically favored at low temperatures. The Gibbs free energy (27) of the reactions favor the formation of carbonates until at elevated temperatures (~400⁰ C, 1 bar) the equilibrium shifts towards free carbon dioxide. However, the

direct solid-gas reaction rates for known reaction pathways are slow, providing the motivation to search for new more rapid pathways. Such studies are key to CO₂ mineral sequestration cost optimization, since, as a first approximation, process cost is proportional to its reaction time and inversely proportional to the degree of reaction completion.(25) Initial direct solid-gas reaction studies of serpentine by Lackner were able to partially carbonate samples of 100 micron radius to about 25% of the stoichiometric maximum by treating the mineral with CO₂ at 340 bar and 500⁰ C for 2 hours (22). More recent research at the Albany Research Center (29) has focused upon the direct carbonation of olivine coupled with secondary carbonation of the serpentine formed. Initial results for olivine particles in the 75-100 micron range exposed to CO₂ and water at 150-250⁰ C and 85-125 bar for 24 hours indicate that 40-50% of the stoichiometric maximum was carbonated. The literature indicates that it is also possible to carbonate heat-treated serpentine in weak carbonic acid in aqueous solution (28). Current research is focused on the feasibility of direct carbonation at elevated temperatures and pressures. The operative reaction mechanisms and the associated overall kinetics for various magnesium containing minerals as a function of the amount of water present are being investigated.

In processes in which magnesium hydroxide is first formed from the silicates, rapid kinetics are achieved by first extracting magnesium from the ore using concentrated hydrochloric acid. The hydrochloric acid can be recovered in a second step, the hydrolysis of MgCl₂. The end product is magnesium hydroxide that can be carbonated in a direct gas solid reaction. In the first step, forsterite and serpentine dissolve readily in hydrochloric acid. For serpentine the reaction takes the form



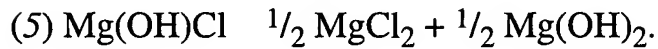
Magnesium enters the aqueous solution exothermically with substantial heat release. MgCl₂ itself is not particularly stable, but is stabilized by forming various hydrates. The different hydrated forms include MgCl₂·H₂O, MgCl₂·2H₂O, MgCl₂·4H₂O, and MgCl₂·6H₂O. The latter is the most stable at room temperature, but at higher temperatures the less hydrated forms are preferred. At 127⁰ C, the hexahydrate transitions to the tetrahydrate and at 182⁰ C the transition to dihydrate occurs. At temperatures between 200⁰ C and 260⁰ C, magnesium chloride hydrolyzes rapidly,



The temperature controls the rate of hydrolysis and the partial pressure of HCl. If the HCl could be kept in aqueous solution the enthalpy of the reaction would be very small. However, there is substantial energy cost in vaporizing the HCl.

In a non-hydrated process, the resulting product is Mg(OH)Cl, whereas in an aqueous process one may be able to make Mg(OH)₂ directly. Mg(OH)Cl can react to form the chloride and hydroxide in aqueous

solution according to the following reaction



Since the hydroxide is insoluble, it should be straightforward to separate the two components. Unfortunately, the thermodynamic predictions only allows the above reaction to proceed under conditions which yield the hexahydrate, implying that the reactants need to be fully hydrated again. Whether produced directly or from Mg(OH)Cl, magnesium hydroxide is forwarded to the final carbonation step, which proceeds readily at elevated pressure and temperature.

For the purposes of CO₂ disposal, heat management is critical. If the overall energy consumption approaches the energy originally generated from the fossil fuel, the process has no value. More than just optimizing heat flows, thermodynamic descriptions (30-32) of MgCl₂ melts allow consideration of significant modifications to the baseline process. Such modifications are indeed believed necessary, because the baseline process involves large amounts of water evaporation and condensation, and the temperatures and pressures are arranged such that heat cannot be completely recovered internally without substantial compression work (25).

The current approach under investigation is to reduce the amount of water vaporized in the cycle, which requires at least some departure from the original process sequence. One way of achieving this is to operate the dissolution step with less water, but at higher temperature to maintain the liquid state. This has the added benefit of reducing the pressure that must be maintained in the process vessel. For example, the water vapor pressure over molten MgCl₂·4H₂O is only 1 bar at 190⁰ C. The heat of condensation of water vapor and HCl gas can then also be recovered in the same step, requiring only minimal vapor recompression. It may also be possible to lower the amount of water vaporized in the cycle, if Mg(OH)Cl or Mg(OH)₂ can be precipitated from magnesium chloride melt without substantial dehydration.

The modifications that have been considered are all motivated by the need to reduce the amount of water evaporation and condensation to improve process efficiency. Some evaporation is necessary, since the MgCl₂ solution, produced from mineral dissolution or elsewhere in the process, must be almost completely dehydrated in order to regenerate HCl through hydrolysis. The first questions to be addressed are whether the key steps of the baseline process, namely mineral dissolution and repartitioning of MgOHCl, can be operated in more concentrated and higher temperature melts. Generally the reactions to be considered involve the MgCl₂ melt or its components as reactant, product, or intermediate. Therefore, the thermodynamic descriptions of the melt have been completed (30-32) to decide whether potential reactions are allowed or forbidden, and under what circumstances of pressure, temperature, and concentration they may occur. The next critical step in optimizing the use of MgCl₂ melts for mineral carbonation is the experimental verification of the thermodynamic calculations and the determination of

the actual kinetics.

Regardless of which hydration state is utilized in any version of the aqueous process, fundamental studies on the mechanisms of formation of Mg(OH)₂ and Mg(OH)Cl and their subsequent carbonation to MgCO₃ are critical to overall carbonation reaction process optimization. Early results on the carbonation of the hydroxide suggest that both the nature of the hydroxide feedstock (e.g., its crystallinity and crystal grain size, the type, concentration and location of structural defects present, and the type, concentration, and location of impurities present) and the presence of water have a direct consequence on the kinetics of the carbonation (21). Investigations are currently underway to identify the key mechanisms that govern gas-solid Mg(OH)₂ carbonation kinetics. The goal is to provide atomic-level insight for engineering improved carbonation materials and processes for CO₂ disposal (33).

Issues to be Addressed

Despite the many advantages discussed above, mineral carbonation processes will only be practical when two key issues are well addressed. First, natural carbonation processes are very slow. For sequestration purposes, a fast reaction route that does not consume a significant amount of energy, preferably generating net energy, must be found. To achieve this goal, the reaction mechanisms, kinetics and specific heat requirements of the individual steps of each process must be understood well enough to permit economic and engineering process optimization. Second, mining is an environmentally sensitive practice. Issues with respect to the mining and processing activity needed for mineral sequestration need to be quantified, especially concerns related to overall economics and environmental impact. These two issues are discussed below.

Reaction Kinetics and Heat Utilization

While overall carbonation reactions are thought to be qualitatively understood, detailed physio-chemical mechanisms are far from being precisely defined. Although data on individual processing steps are essential to defining their optimum configuration, ultimately, the keys to the success of mineral carbonation lie in the kinetics of the overall reaction process. The reactions must be completed in time frames that are acceptable for large-scale processing equipment. Although the overall process is exothermic, the heat requirements for specific steps in any envisioned process must be addressed in an integrated manner in order to maximize total process heat recovery and utilization.

Mining and Processing

Excluding environmental acceptability, which is a prerequisite, perhaps the single most important criterion for the use of a mineral carbonation process to sequester CO₂ is the associated economics of the process. While a thorough economic review is required, a quick review of mineral processing economic studies implies that the process has potential. Data on the mining of olivine, a suitable magnesium silicate for mineral carbonation, indicate that today, small-scale operations, 1-2 MMT (million metric tons) per year produce olivine at prices quoted between \$50-\$100 per ton (34). Copper production, which can be used as a reference for similar large-scale production, provide cost estimates (based upon 1990 figures) which appear to average \$7 per ton of ore, although costs as low as \$4/ton are found. Alternatively, comparisons to smaller scale asbestos mining take into consideration mining and milling costs for serpentinite and any specialized equipment needed to deal with potential particulate exposure during the mining and milling operations, such as specialized air handling equipment. These estimates indicate operating costs for mining and milling (both direct and fixed costs) to be nearly \$9 per ton of ore at an operating scale of nearly 20,000 tons per day (35). Note, to provide a basis for comparison, ~50,000 tons/day is required to match what is needed for mineral carbonation for a 1 Gigawatt electric power plant operating at 33% efficiency. A cost of \$10/ton of CO₂ sequestered corresponds to a cost increase of 0.9 cent/kW-hr at a typical coal fired power plant (33% efficiency). As the efficiency of power plants is increased, that number will go down.

The actual costs associated with the mineral carbonation process will be dependent upon the composition and location of specific mineral bodies (Mg content, reclaimed values, distances to power plants, etc.), the economies of scale that can be applied, and the specific processes that must be utilized for processing the specific mineral bodies. Co-production of valuable byproducts such as iron is also a possibility in certain carbonation schemes.

Environmental Issues

It is anticipated that any new disruption of the environment, even if far less severe than existing ones, will cause much more controversy than those already existing. It is critical that environmental issues be identified and fully addressed up front.

Environmental issues will pertain to specific proposed mine sites. Mining and milling operations have the potential for liberating respirable particulates. Methods have been adopted by the mining industry to reduce or eliminate liberation of such particulates. Most of the effort has focused on milling operations, where an order of magnitude more air borne particulates are generated. Regardless of the ability to contain the respirable particulates, public perception and local resistance have the potential to delay, stop, or add significant costs to the mining operation, or any other CO₂ disposal method, and, thus, must be well characterized.

Waste issues from the carbonation process pose several questions that must be addressed. The first issue

relates to the volume of material that is generated. Estimates of a 40 percent volume increase after processing poses a problem in materials disposal. This is a critical issue since most of the materials for disposal will be particulates.

Insoluble materials, which will be present in any mineral ore, will be concentrated during processing. Even trace concentrations of 1 part per million will produce 18 tons of a contaminant per year in a 50,000 ton per day operation. Contaminants must therefore be completely characterized to determine the potential of generating a hazardous waste in the insoluble fraction of the ore or, hopefully, providing a source of potentially valuable materials.

These environmental concerns (particulate emissions in the mining and milling operations, the volume increase between the input silicates and the output stream of carbonates and silica, the need to physically stabilize this material, and the potential need to handle other waste products associated with the overall process) must be addressed in addition to the technical feasibility to operate the carbonate formation process proposed. Public opinion and concern about trading one potential environmental problem (CO₂) for a known undesirable activity (large-scale open-pit mining) must be recognized and addressed. It should also be weighed against the less well understood environmental impacts of other sequestration methods.

Program Implementation

Current projects are examining the technical and economic feasibility of CO₂ sequestration as mineral carbonates by using a multi-laboratory approach to generate the underlying technical and economic data required to allow process definition and optimization and to search for and investigate fundamental processing options.

Technical Issues

Research activities are focused into three major areas in order to achieve program goals, and address first-order technical, economic, and environmental concerns. First, the different carbonation methods need to be much more fully developed and examined relative to the overall thermodynamics and kinetics of proposed processes. For example, fundamental mechanisms related to rate determining steps are currently being addressed for the aqueous approach since rapid reaction kinetics have been demonstrated and need to be further understood in order to optimize the aqueous carbonation method. Note that investigations of fundamental carbonation mechanisms is now limited by budget constraints. Second, system feasibility needs to be examined from both economic and environmental perspectives and fed back into the process development. Finally, feedstock characterization needs to be conducted to determine all appropriate sources of Mg and Ca bearing minerals (although Ca is generally more expensive to extract due to its typically lower concentration in mineral deposits, these minerals will also

be evaluated since Ca is often present in Mg bearing minerals and can also be effectively used for CO₂ sequestration) (17) and the specific processing steps to integrate mineral/waste recovery into the carbonation process.

Researchers at the Albany Research Center (ARC), Arizona State University (ASU), the Federal Energy Technology Center (FETC), and Los Alamos National Laboratory (LANL) are currently engaged in mineral carbonation research. Projects address all of the program areas and are focused on the key problems relative to the technical, economic, and environmental issues discussed above. In the early stages of the research effort, and especially in the areas of thermodynamic and kinetic parameter determination, a degree of experimental overlap will take place. This will serve to strengthen confidence in the values obtained for these critical parameters and to establish a common basis for future work

Note that several activities necessary to evaluate the absolute viability of mineral sequestration will not be investigated here. While it is readily recognized that activities such as life cycle analyses, risk assessments and ecosystem interactions studies are essential before proceeding with the wholesale deployment of any large-scale, resource intensive industrial process, the phase I feasibility study undertaken here does not warrant this level of effort. These activities are left for latter stages of process development that might be warranted based on the results obtained in the initial fundamental studies.

Current Projects

Carbonation Reactions

1.) Direct Carbonation of Mineral Silicates

The purpose of these experiments is to find economically accessible parameter ranges in which the direct reaction between magnesium silicates and carbon dioxide goes to completion and proceeds rapidly. The reactions will involve water, carbon dioxide and a mineral silicate. Both pure and natural samples that contain typical impurities will be studied. Initial experiments at LANL and ARC of this type have already been performed and their partial success provides the basis and justification for a more detailed exploration. The following two areas will be explored in detail:

- i. Supercritical carbon dioxide plus water plus silicate powder as function of silicate grain size and water content.
- ii. Carbon dioxide/steam reaction mixtures as a function of partial pressures and temperatures over the regime from 5 bar to 50 bar and 200 to 700⁰ C.

If successful at the higher temperature range, the reaction would generate a useful amount of energy that could be captured in a power plant.

2. Molten Salt Carbonation

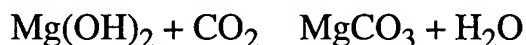
The system MgCl_2 B H_2O B HCl B $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ B CO_2 , in a regime in which H_2O and (most likely) HCl concentrations are small, and where CO_2 may or may not be present will be studied. Thermodynamic calculations suggest it is worthwhile to investigate these reactions. The thermodynamic calculations need to be verified by experiments, particularly in those cases where high pressures and temperatures are involved and the existing thermodynamic values have relatively large error bars. In addition, the effect of impurities in the serpentine must be quantified and issues associated with separation of the SiO_2 and MgCO_3 from the melt must be addressed.

3.) Aqueous Systems

A substantial understanding of the direct carbonation of $\text{Mg}(\text{OH})_2$ has been gained from previous experiments at LANL. Increasing the reaction rate would help in reducing the cost of the process. Production of $\text{Mg}(\text{OH})_2$ as a carbonation reaction intermediate may be of interest in some cases even if the direct carbonation of mineral silicates proves to be a feasible process. The advantages of using $\text{Mg}(\text{OH})_2$ include:

- i. It may still be the method of choice for olivine.
- ii. Fluidized beds integrated into the power production system may prefer a chemically less aggressive material like $\text{Mg}(\text{OH})_2$ over the acidic chloride melt.
- iii. Investigations of processes for absorbing CO_2 from air that may work with $\text{Mg}(\text{OH})_2$ will need this information.

Consequently, the reaction



in the presence of excess water will be studied. The goal is to improve the efficiency of the aqueous process.

4) Atomic-Level Imaging of the Reaction of CO₂ with Mg(OH)₂: Optimizing Reaction Process Design

Direct gas-solid carbonation of Mg(OH)₂ offers the potential advantage of being able to capture the reaction energy in concentrated form allowing it to be used in earlier process steps. Fundamental research is being performed to develop an atomic-level understanding of the mechanisms that govern the kinetics of the complex Mg(OH)₂ carbonation process to facilitate engineering of improved carbonation materials and processes. Similar work will be required for any alternative reaction pathway. Therefore, the scope of this work will be expanded in the future.

System Feasibility

1.) Economic Considerations

Studies of various areas related to the overall concept from an engineering point of view are required to address potential process costs. Where possible, cost estimates for various unit operations (such as the required mining of the "virgin" minerals, disposal of the "product" minerals, capital and operating costs of the pressure leaching/gas absorption steps, *etc.*) are needed. In order to assess the potential viability of proposed processes using various minerals as materials to sequester carbon dioxide from fossil fuel-fired power plants, the following areas are to be studied:

i) An assessment of the mining approaches that are necessary to recover the minerals from the ground and the required processing of the minerals (such as, crushing, grinding, and sizing). Also, the ratio of waste material to the desired mineral(s), the "order of magnitude" of the waste mining products generated, and the impurities within the desired minerals will be evaluated. This will be used to forecast the level of hazardous wastes that might be generated related to the mining operation or in subsequent processing that would add extra costs to the operation. Given the greater weight of the serpentine rock required relative to that of the coal consumed and the likely disposal of the carbonates in the open pit mine from which the serpentine originated, the disposal plant would be located at the site of the serpentine mine. As such, only the mining, processing, local transportation, and land reclamation costs would be estimated. This part of the study will be based on four or more deposit sites that will be selected based upon their size (large), their proximity to potential power plant users, and whether their mineral content and deposit geometry matches the majority of similar deposits.

ii) Overall material balances for the major required inputs and outputs for the proposed processes. For example, what is the required consumption of water for a

reasonably sized carbon dioxide sequestration plant? This feature alone may dictate where sequestration plants can be located, or which mineral deposits would be utilized. Also of concern is how much waste material or low-value byproduct (including the carbonated minerals and iron oxide) would be produced and have to be disposed of or utilized?

iii) Overall energy balances for all of the required operations. Currently proposed processes would require mining operations, mineral processing such as grinding, the local transportation of large amounts of materials (minerals, byproducts, wastes), heating of solutions and slurries, pumping and compression of various phases, drying of materials such as wastes, all at a very large scale. Almost all of these operations will directly or indirectly generate carbon dioxide themselves. Therefore, the overall impact of the operations and the associated costs need to be estimated.

2.) Disposal of Waste

An assessment of the potential environmental impacts related to these approaches will be made. Since the LANL aqueous process is best defined at this point, the following discussion is directed toward that process. Similar issues will likely arise with direct carbonation and molten salt approaches and will be studied as these processes are developed. Initial studies will therefore be focused to help find appropriate methods for handling the iron and silica streams of the aqueous process. That information will then be incorporated into the engineering study of the aqueous mineral sequestration process and appropriate cost evaluations will be completed.

3.) Recoverable Values

Research will be conducted to obtain an understanding of the disposition (and potential importance) of trace impurities in the minerals and possibly the off-gases within the sequestration processes. For example, it is likely that toxic impurities such as chromium, mercury, and/or molybdenum will be contained in the minerals to be used for sequestration. Both theoretical and laboratory studies will be made to estimate where these (and other) impurities will distribute themselves within the various unit operations. Possible methods of dealing with those impurities, including recovery and use, will be made and (where possible) related cost evaluations or cost impacts will be made.

Feedstock Characterization

Mineral Characterization

Mineral deposits in the western U.S. are fairly well characterized. However, an

assessment of the availability of minerals east of the Mississippi River that would be needed for the processes will be conducted. This includes quantification of the mineral resources and identifying their proximity to current power plants and/or fossil fuel deposits. Knowledge of specific mineral deposit characteristics and chemical compositions are required to obtain realistic economic assessments, to develop overall processing approaches, and to determine their associated potential recovery values and environmental impacts.

Primarily through outreach activities, additional efforts will be made to identify high volume, low- or negative-value, Mg- and Ca- containing industrial residues, which may serve as feedstock materials.

Concluding Remarks

The planned research is just beginning to explore the potential of mineral carbonation for CO₂ sequestration. It can be anticipated that new approaches and strategies may be needed. Other issues to be addressed include additional research, funding, stakeholders, etc.

Additional research

Reaction chemistry

Little is known about the energy barriers in the various carbonation reactions, except the aqueous ones. Examination of the detailed mechanisms and the fundamental reaction chemistry that governs these reactions and their associated energy barriers and kinetics is needed.

Role of catalysts

Since most of the nonaqueous carbonation reactions are slow, especially at ambient conditions, it would be useful to seek the help of catalysts.

Separation of reaction products

Separation of products is an issue for several of the processes. In the molten salt process, the separation of the carbonate and silica from the salt is likely to be troublesome, and in aqueous processes the possible problem of the silica gels looms. In addition, successful separation of useful byproducts such as iron or other metal ores can provide valuable byproducts for the metallurgical industry, significantly enhancing the economic viability of the overall process.

Stakeholders

There are many potential stakeholders in this program. Apart from the electric utilities, coal producers and their associations as potential beneficiaries, other major stakeholders include the mining industry which would produce the CO₂-binding minerals. In addition, chemical and metal manufacturers could potentially use some byproducts from mineral sequestration as inexpensive feedstock, or be able to dispose of some of their waste stream via the mineral sequestration process.

The knowledge generated in studying mineral carbonation will also benefit other sequestration studies such as geological ones. The injection of CO₂ into saline aquifers would benefit from knowledge of CO₂/mineral reaction processes. Similarly, reaction data of CO₂ with different minerals would also be useful in analyzing the long-term stability of CO₂ storage in gas or oil reservoirs.

In summarizing this discussion, one must be reminded that although the study of mineral carbonation is still in the early stage, its significant merits such as long term stability and vast capacity make it an appealing approach in reducing CO₂ emissions. The sequestration is permanent, ensuring a continued ability for fossil fuels to provide for the world's energy demands through the 21st century and beyond.

REFERENCES

1) U. Siegenthaler and H. Oeschger, *Atmospheric CO₂ Emissions During the Past 200 Years Reconstructed by Deconvolution of Ice Core Data*, *Tellus* **39B**, 140-154 (1987).

C.D. Keeling, T.P. Whorf, M. Wahlen, and J. van der Plicht, *Interannual Extremes in the Rate of Rise of Atmospheric Carbon Dioxide since 1980*, *Nature* **375**, 666-670 (1995).

EIA (Energy Information Administration) 1999, *International Energy Outlook 1999*, DOE/EIA-0383(99), U.S. Department of Energy, Washington, D.C.

S.I. Plasynski, C.B. Bose, P.D. Bergman, T.P. Dorchak, D.M. Hyman, H.P. Loh, and H.M. Ness, *Carbon Mitigation: A holistic Approach to the Issue*, Paper presented at the 24th Intl. Tech. Conf. On Coal Utilization and Fuel Systems, March 8-11, 1999, Clearwater, FL.

United Nations, *1991 Energy Statistics Yearbook*, New York, 1993.

Vision 21, *Clean Energy for the 21st Century*, U.S. Department of Energy, Office of Fossil Energy DOE/FE-0381, November, 1998. (Also available on www.fetc.doe.gov/publications/brochures/)

7) W. R. Collings & J. A. Gann, *A Method of Making Anhydrous Magnesium Chloride*, United States Patent Office, Patent 1,479,982, January 8, 1924.

- 8) A. K. Smith, AMethod of Preparing Magnesium Chloride from a basic Chloride Thereof,@ United States Patent Office, Patent 1,880,505, October 4, 1932.
- 9) A. K. Smith & W. R. Veazey, ADehydration of Magnesium Chloride,@ United States Patent Office, Patent 1,874,373, August 30, 1932.
- 10) E.A. Gee, C.E. McCarthy, F.S. Riordan, Jr., and M.T. Pawel, "Magnesia from Olivine," U.S. Department of Interior, Bureau of Mines, Report of Investigation 3938, September 1946.
- 11) E.C. Houston, "Magnesium from Olivine," A.I.M.E. Tech. Pub., No. 1828, **85**, 1-14, 1945.
- 12) Virgil E. Barnes, D. A. Shock and W. A. Cunningham, AUtilization of Texas Serpentine,@ The University of Texas, Publication No. 5020, October 15, 1950.
- 13) W. Seifritz, ACO₂ Disposal by Means of Silicates.@ *Nature*, **345**, 486 (1990).
- 14) T. Kojima, A. Nagamine, N. Ueno and S. Uemiya, AAbsorption and Fixation of Carbon Dioxide by Rock Weathering.@ Proceedings of the Third International Conference on Carbon Dioxide Removal, Cambridge Massachusetts, September 9–11, 1996, *Energy and Conservation Management*, **38 Suppl**, S461–S466 (1997).
- 15) Stefan Bachu, W. D. Gunter and E. H. Perkins, AAquifer Disposal of CO₂: Hydrodynamic and Mineral Trapping.@ *Energy Conversion and Management*, **34**, 269–279 (1994).
- 16) William D. Gunter, Ernest H. Perkins and Tom J. McCann, AAquifer Disposal of CO₂ rich gases: Reaction Design for Added Capacity.@ *Energy Conversion and Management*, **34**, 941–948 (1993).
- 17) K. S. Lackner, C. H. Wendt, D. P. Butt, D. H. Sharp, and E. L. Joyce, "Carbon Dioxide Disposal in Carbonate Minerals," *Energy (Oxford)*, **20** [11] 1153-1170 (1995).
- 18) F. Goff and K.S. Lackner, "Carbon Dioxide Sequestering Using Ultramafic Rocks," *Environmental Geosciences*, **Vol. 5**, Number 3, 89-101, 1998.
- 19) K. S. Lackner, D. P. Butt, C. H. Wendt, ACarbon Dioxide Disposal as Mineral Carbonate,@ *Energy Convers. Mgmt.*, **38**, S259-S264 (1997).
- 20) D. P. Butt, K. S. Lackner, C. H. Wendt, Y. S. Park, A. Benjamin, D. M. Harradine, T. Holesinger, M. Rising, and K. Nomura, AA Method for Permanent Disposal of CO₂ in Solid Form,@ *World Resource Review*, **9** [3] 324-336 (1997).

- 21) D. P. Butt, K. S. Lackner, C. H. Wendt, S. Conzone, H. Kung, Y.-C. Lu, and J. K. Bremser, "Kinetics of Thermal Dehydroxylation and Carbonation of Magnesium Hydroxide," *J. Am. Ceram. Soc.*, **79** [7] 1892-1898 (1996).
- 22) D. P. Butt, K. S. Lackner, C. H. Wendt, A. S. Benjamin, D. M. Harradine, T. G. Holesinger, Y. S. Park, and M. Rising, "A Method for Permanent Disposal of CO₂ in Solid Form," to be published in *Waste Management Technologies and the Ceramic and Nuclear Industries*, Ceramic Transactions, American Ceramic Society, Westerville, OH, 1998.
- 23) K. S. Lackner, D. P. Butt, and C. H. Wendt, "Magnesite Disposal of Carbon Dioxide," *Proceedings of 22nd International Technical Conference on Coal Utilization and Fuel Systems*, pp. 419-430, Coal and Slurry Technology Association, Washington, D. C., 1997.
- 24) K. S. Lackner, C. H. Wendt, D. P. Butt, and D. H. Sharp, "Carbon Dioxide Disposal in Solid Form," *Proceedings of 21st International Technical Conference on Coal Utilization and Fuel Systems*, B. A. Sakkestad editor, Coal and Slurry Technology Association, Washington, D. C., pp 133-144, 1996.
- 25) K. S. Lackner, D. P. Butt, C. H. Wendt, F. Goff, and G. Guthrie, "Carbon Dioxide Disposal in Mineral Form: Keeping Coal Competitive," Los Alamos National Laboratory Report, LAUR-97-2094, 1997.
- 26) K. S. Lackner, D. P. Butt and C. H. Wendt, "The Need for Carbon Dioxide Disposal: A Threat and an Opportunity," To appear in the Proceedings of the 23rd International Conference on Coal Utilization & Fuel Systems, Clearwater Florida, March 1998.
- 27) Richard A. Robie, Bruce S. Hemingway & James R. Fisher, "Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures," U. S. Geological Survey Bulletin 1452, reprinted with corrections 1979.
- C. Drăgulescu, P. Tribunescu & Olga Gogu, "Lösungsgleichgewicht von MgO aus Serpentin durch Einwirkung von CO₂ und Wasser," *Revue Roumaine de Chimie*, **17**, 9, 1518-1524 (1972)
- 29) W. K. O. Connor, "Investigations into Carbon Dioxide Sequestration by Direct Mineral Carbonation." Presentation at Second Meeting of Mineral Sequestration Working Group, November 3, 1998, Albany Research Center, Albany, Oregon.
- 30) C.H. Wendt, D.P. Butt, K.S. Lackner, and H-J Ziock, "Thermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts- I: Description of Concentrated MgCl₂ Melts," Los Alamos National Laboratory Report, LAUR-98-4528, July 27, 1998, 22 pp.
- 31) C.H. Wendt, D.P. Butt, K.S. Lackner, and H-J Ziock, "Thermodynamic Calculations for Acid

Decomposition of Serpentine and Olivine in MgCl₂ Melts- II: Reaction Equilibria in MgCl₂ Melts.® Los Alamos National Laboratory Report, LAUR-98-4529, October 7, 1998, 28 pp.

32) C.H. Wendt, D.P. Butt, K.S. Lackner, Raj Vaidya, and H-J Ziock, AThermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts- III: Heat Consumption in Process Design.® Los Alamos National Laboratory Report, LAUR-98-5633, November 25, 1998, 23 pp.

33) M. J. McKelvy, R. W. Carpenter, R. Sharma, and K. Streib, AAtomic-Level Imaging of CO₂ Disposal as a Carbonate Mineral: Optimizing Reaction Process Design.® Presentation at Second Meeting of Mineral Sequestration Working Group, November 3, 1998, Albany Research Center, Albany, Oregon.

34) D.R. Wilburn, AMagnesium Availability-Market Economy Countries, A Minerals Availability Appraisal.® Bureau of Mines Informtion Circular 9112, 1986, 24 pp.

35) R. G. Bottge, AComparative Asbestos Mining and Processing Costs-Alaska Versus Yukon Territory.® Bureau of Mines Information Circular 8672, 1974, 33 pp.